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THE BEHAVIOR OF AN IRON ELECTRODE
IN ALKALI SOLUTIONS AT LOW TEMPERATURES

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8 August 1946

It is known that an electrode* pressed from powdered iron serves as the cathode in an Edison battery. The behavior of this electrode at low temperatures is distinguished by a number of peculiarities. In particular, the basic characteristic of the electrode, its capacity (expressed in ampere-hours), greatly decreases with a lowering of temperature, and at -25 to -30 degrees the electrode almost completely breaks down. Since a Jungner-type ferrocadmium electrode works at these temperatures, the cause of the loss of capacity may be considered to be in the change of the properties of these electrodes at low temperatures. This effect cannot be explained by the change of the properties of the solution because the latter is the same in both cases. This work will attempt to explain the cause of the loss of capacity of an iron cathode at low temperatures.

Research Method

The tests were made in an apparatus constructed similarly to that described in the work of Lukovtsev, Levine, and Frumkin (Zhurn. fiz. khimii 13, 916, 1939). The apparatus was considerably smaller in order that the entire apparatus could be placed in a 10-cm diameter Dewar flask for the low-temperature tests. Pure powdered iron pressed under 1,000 atmospheres was the object of study. A solution of caustic potash with a specific gravity of 1.28 - 1.30, i.e., an optimum concentration for work at low temperatures, was used as the electrolyte. A Dewar flask with a mixture of alcohol and solid carbonic acid served as a cryostat.

Results of the Measurement And Discussion

Curves of cathodic and anodic polarization at +20 degrees C and -30 degrees C

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are shown in Figure 1. (all values of potentials are given with reference to the reversible hydrogen electrode in the same solution and at the same temperature). The curve at a low temperature in the field of hydrogen overvoltage has a steeper slope and lies 160 mv higher, i.e., the temperature coefficient of overvoltage is 3 mv more per degree. The anode curve also is steeper and intersects the abscissa at a current lying approximately one order of magnitude lower than at room temperature.

At very low and no-current potentials, the following phenomenon is observed. At -30 degrees, as is seen from the graph, the steady potential is 80 mv more negative than at 20 degrees. Upon connecting the current, the potential maintains a high negative value for some time and then gradually falls and stops at a potential approximately 20 mv more negative than at 20 degrees. A high negative value of the steady potential is observed if the cooling is carried out in the presence of a current; in the case studied, the current had a strength of several milliamperes. If, however, the cooling is carried out without a current, this potential has a more positive value than at room temperature, but nevertheless it is more negative than the hydrogen. However, if the electrode is subjected to cathodic polarization even with a very small current, the value of the potential sharply changes to the negative side and, with a further increase of the current, follows a curve which is obtained when a measurement is made from this large to small values with cooling in the presence of a current.

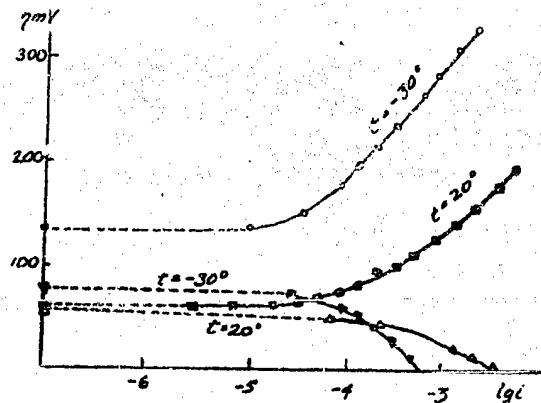


Figure 1. Cathode (O, C) and Anode (Δ) Curves on Powdered Iron at +20 and -30°C.

The curves of cathodic polarization at +20 degrees and -30 degrees C on smooth iron are compared in Figure 2. As for the powdered electrode, here also the temperature coefficient is approximately 3 mv per degree. The path of the curve is steeper with a slope of 0.12. Apparently this is due to the fact that the measurements on the smooth electrode are made in a field of considerably greater densities of current. With regard to the no-current potential at -30 degrees, it is 16 mv more negative than the reversible, but more positive than at room temperature.

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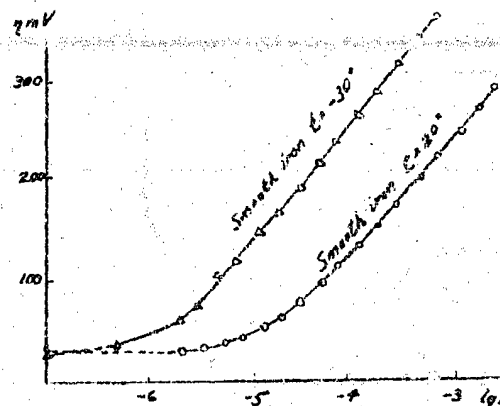


Figure 1. Cathode Curves on Smooth Iron at +20 and -30°C.

Comparison of the curves at room and low temperatures leads to the following results. First, the path of polarization curves at low temperatures has a noticeably steeper slope. Second, the temperature coefficient of overvoltage is more than 3 mV per degree, which is abnormally great for this interval of current density.

This data forces us to suppose that at low temperatures there is a film of oxides or adsorbed oxygen on iron, even with negative potentials. As Richards and Behr (Ztschr. Physik. Chem. 58, 301, 1907) have already shown, the potential of the iron electrode in a solution of its salts in an atmosphere of hydrogen is established very slowly as a result of the difficulty of separating oxygen from the surface of the electrode. At low temperatures the kinetics of this process are probably slowed down even more and oxygen forms a stable layer of oxides on the surface of the iron electrode. Apparently the influence of this layer expresses itself both in steeper polarization curves and in a comparatively high value of the temperature coefficient of overvoltage. (It is known from the work on evolution of gas on iron that if a small amount of oxygen remains on the surface of a cathode after restoration, the overvoltage sharply shifts to the negative side and the whole curve has a considerably steeper slope.) The nature of this film remains unexplained. On the one hand, it can be looked upon as a disequilibrium formation which results from the oxidation of iron by traces of oxygen in the solution and which is not removed in cathodic polarization because of the slowness of the restoration process at a low temperature. On the other hand, it is possible to suppose that with a decrease in temperature and with practically realizable potentials and a complete absence of molecular oxygen in the system, both the bonding stability of the oxygen and its amount on the surface increase. The experimental data which we have at present is insufficient to make a choice between these two suppositions. It is entirely probable that the film, stable at a low temperature and less stable at room temperature, not only increases the overvoltage, but also passivates the iron, causing the sharp decrease in capacity of the iron cathode at low temperatures.

Considering the dual action of the oxide film, it is possible to explain the particular changes of the steady potential at high temperatures on the powdered and smooth iron which are described above. An increase of the overvoltage causes a shift of the steady potential to the negative side, and passivation

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of the anode process to the positive side. In the case of a powdered electrode, the shift of the steady potential and the currentless potential to the negative side can be treated as the first stage of action of the oxide film. In the case of an electrode without a current, the passivation is increased and the potential gradually shifts to the positive side, but nevertheless remaining somewhat more negative than at room temperature. If, however, the cooling is done without a current, the passivation of the electrode becomes considerably stronger and its potential acquires a value which is more positive than at room temperature. In the case of a smooth electrode the passivation becomes faster and its steady potential at a lower temperature always has a more positive value than at room temperature.

For a further explanation of the role of the passivating film at low temperatures, curves of discharge and charge at room temperature and at -25 degrees were compared. It is already known from the classic works of Foerster (Ztschr. Elektrochem. 16, 461, 1910) that in the discharge of an iron electrode at a constant current, a horizontal platform corresponding to the reaction $\text{Fe} \rightarrow \text{Fe}^{++}$ is observed, after which the potential sharply shifts to the positive side and a new platform, corresponding to the transfer from Fe^{++} to Fe^{+++} appears. The amount of ampere-hours which is passed through the electrode before reaching the end of the first platform characterizes the capacity of the electrode. The normal capacity of an electrode of average activity at room temperature is approximately 0.2 ah per gram of iron with a current of 25 ma per gram. At -25 degrees the capacity of the iron electrode decreases by 10 percent of this magnitude. According to numerous experiments, if discharge at a low temperature is made down to a potential 400 mv more positive than the reverse hydrogen and even considerably farther, and then the discharge current is disconnected and the cooling stopped, the potential quickly returns to a stationary value. In the subsequent connection of an anode current at room temperature the remaining capacity, which is unused at the low temperature, is spent.

On the basis of the peculiarities expressed above of the presence of an oxygen film on iron at low temperatures, it was decided to modify the described experiment by not disconnecting the discharge current after stopping the cooling in order that the passivating layer of oxides would not have the possibility of restoring itself.

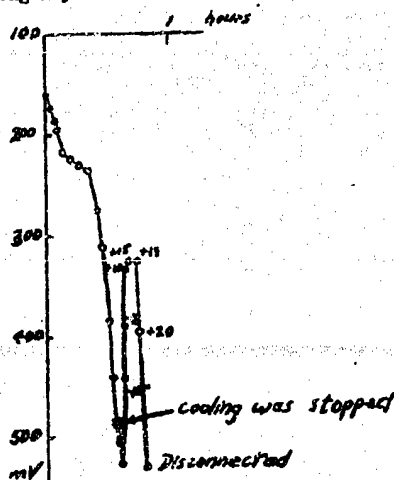


Figure 3. Curve of the Discharge of an Iron Cathode at -25°C with Heating by a Connected Anode Current

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Actually, if the cooling is stopped and the apparatus is submerged in the water at room temperature (direct measurements with a thermometer placed inside the apparatus show that room temperature is set up in the apparatus 5-6 minutes after removal of the cryostat and its replacement by a water bath at room temperature) and at the same time the discharge current is not disconnected, then the potential at first shifts a little to the negative side, and then again quickly returns in the direction of positive values. The curve obtained in a discharge current of 3.5 ma and a temperature of -25 degrees is presented in Figure 3. The discharge was carried down to a potential 520 mv more positive than the hydrogen. At this moment the cooling was stopped and the apparatus was submerged in a water bath at room temperature with the anode current unconnected. The path of change of the temperature is marked in separate points along the potential curve. It is seen from the drawing that the potential at the beginning changed from 525 to 320 mv more positive than the hydrogen, and then began again to shift steeply to the side of negative values. Analogous tests were compared also for other values of the discharge currents. The smaller the discharge current, the greater is the shift to the negative side after stopping the cooling. Apparently the shift to the negative side is connected with an increase of the electrochemical activity of the iron in heating. However, if sufficient passivating oxides have accumulated on the surface of the electrode in the discharge, then their quantity continues to increase and at a higher temperature. After some time the potential of the electrode again begins to change to the positive side. If the discharge is made by a small current and not allowed to shift greatly from the potential value of the horizontal platform, then in spite of the continuing discharge, the potential quickly reaches a steady value upon heating to room temperature, and the capacity which is not used at the low temperature is removed. Thus, the test of warming up the electrode under conditions of connected discharge current confirmed the hypothesis expressed above that the cause of the lowered capacity at low temperatures is the presence of an oxide film on the surface of the iron electrode.

The role of an oxygen passivating film at low temperatures is also confirmed by observations of the magnitude of the temperature coefficient of overvoltage of iron at various temperature intervals. In distinction from other metals (according to literature data), powdered iron has entirely peculiar dependence of the temperature coefficient upon the temperature. A comparison of the temperature coefficients was made for comparatively large values of current, but in a limited interval, according to the following consideration. On the one hand, at low temperatures it is impossible to measure the value corresponding to a high current density because of the decreasing electrical conductivity. On the other hand, at high temperatures the curve for small currents is greatly altered as a result of the increasing solubility of the iron, and a normal curve of overvoltage is obtained only with comparatively high values of currents.

Measurements were made in an interval from +50 to -20 degrees C. The results are presented in Table 1.

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Table 1

Dependence of the Coefficient of Overvoltage upon the Temperature
 η - overvoltage, i - strength of the current,
 t - temperature

$t_1 - t_2$	$i = 16 \text{ ma}$	$i = 3 \text{ ma}$
50 - 40	1.7	-
40 - 30	1.7	-
30 - 20	2.0	-
20 - 10	3.0	2.5
10 - 0	3.8	3.8
0 - (-10)	4.2	4.0
10 - (-20)	-	4.6

It is seen from Table 1 that the sharpest increase of the temperature coefficient is observed at an interval from 20 to 0 degrees. With a further decrease of the temperature the increase of the coefficient continues, but is not so sharply expressed. From +50 to +30 degrees the coefficient is constant. The lower limit of the temperature range in which the coefficient maintains a constant value and the magnitudes of coefficients at different temperatures may fluctuate somewhat, depending upon the preceding processing of the iron.

The particular change of the temperature coefficient of overvoltage of the iron apparently is also related to the presence of a passivating oxide film, which decreases at high temperatures and becomes stable at low temperatures.

The data presented in the present work on the results of discharge at low temperatures and also on the study of the temperature coefficient support the contention that a decrease in the capacity of an iron cathode at low temperatures is due to the thinner formation of a passivating oxide film on its surface under these conditions.

We express our thanks to Academician A. N. Frankin for his interest and valuable direction in carrying out the present work.

Results

1. Polarization curves at room temperature and at -30 degrees are compared.
2. The steeper slope of the overvoltage curve at -30 degrees and the high value of the temperature coefficient of overvoltage force us to suppose the presence of a film of oxides on the surface of the electrode at low temperature.
3. Tests with a heated electrode with an unconnected anode current confirm the supposition of the formation of a passivating film of oxides on the iron at low temperatures.
4. The temperature coefficient of overvoltage from +50 to -20 degrees C is determined. The particular behavior of the change of the coefficient at low temperatures also confirms the hypothesis of the presence under these conditions, of a passivating film of oxides on the iron electrode, which increases the overvoltage.

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